ELECTRIC QUADRUPOLE INTERACTION OF THE OXYGEN MOLECULE

SHARAD LAGU

ELECTRIC QUADRUPOLE INTERACTION

OF

THE OXYGEN MOLECULE

SHARAD LAGU M.Sc.(POONA.)

SUBMITTED IN PARTIAL FULFILMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

MEMORIAL UNIVERSITY OF NEWFOUNDLAND

SEPTEMBER 1968

TABLE OF CONTENTS

ABSTRACT

The intrinsic absorption coefficient of the oxygen molecule for the fundamental vibrational band has been calculated, assuming an electric quadrupole interaction of the molecule with the incident radiation. The quadrupole matrix elements are approximated by a cubic equation in $r = R - R_e$, where 'R' is the internuclear distance and 'R_e' is its equilibrium value. The wave function of the ground state of the oxygen molecule is written in the Born-Oppenheimer approximation, as a product of electronic and nuclear parts. Completely antisymmetrized orthogonalized molecular orbital wave functions are taken for the electronic part, while the nuclear part of the wave function is written as a product of rotational and vibrational wave functions. The simple harmonic wave functions are taken for the vibrational part.

The integrated absorption coefficients for O, Q and S branches and the total integrated absorption coefficient for the whole band, have been calculated. The results due to Bishop, Shapiro and the present investigation are as follows

	Integrated absorption coefficient cm^{-2}/amagat
Bishop	$2.3 \pm 0.9 \times 10^{-3}$
Shapiro	$3.0 \pm 0.23 \times 10^{-4}$
Present	1.45×10^{-4}

These results are discussed at the end.

CHAPTER I

INTRODUCTION

While studying the pressure induced fundamental band of molecular oxygen, which extends over the region of 1400 cm^{-1} to 1800 cm^{-1} , Bishop (1966) found that there is a contribution to the total integrated absorption coefficient which depends on the density of the gas linearly. A similar observation was made by Shapiro (1965). The value of this absorption coefficient was found by Bishop to be 2.3×10^{-3} cm^{-2} $amagat^{-1}$ while Shapiro found it to be 3.0×10^{-4} cm^{-2} $amagat^{-1}$ Bishop attributed this to a magnetic dipole interaction while Shapiro attributed it to impurities such as water vapour, in the gas. The present investigation was undertaken with a view to see if some kind of electromagnetic interaction is responsible for this intrinsic absorption and to estimate its contribution to the absorption coefficient.

As absorption was observed in the infrared region, it is reasonable to assume that the vibrational transition with small Δv, should be taking place and there should be no electronic transition. The electronic transitions giving an absorption in the infrared region would have been possible if there were low lying excited states or if the temperature were so high that the excited states were sufficiently populated. In our case, the first excited electronic state of the oxygen molecule lies 7918 cm^{-1} above the ground state.(Herzberg, Spectra of Diatomic Molecules, 1964, p.560.) Further, at 298^{o} K almost all the molecules are in the ground electronic state. In this case, therefore, we reject the possibility of the electronic transition contributing to the

absorption in the infrared region.

Now, being a homonulcear diatomic molecule, there is no possibility of an electric dipole interaction in the case of the oxygen molecule, unless such a dipole is induced by some external agency such as pressure. One should therefore consider magnetic dipole or electric quadrupole interactions. The oxygen molecule in the ground state has a magnetic dipole due to the spin. Its electronic ground state is known to be $^3\Sigma_g^-$. The magnetic dipole matrix elements for the transition desrribed above will be

$$\int \psi_e^* \psi_{v'}^* \psi_{j'}^* \bar{\mu} \psi_e \psi_v \psi_j d\Gamma_e d\Gamma_v d\Gamma_j$$

where

μ = magnetic dipole operator

ψ_e = eelectronic part of the wave function of the molecule

ψ_v = initial vibrational part of the wave function

ψ_j = initial rotational part of the wave function,

and primes denote corrosponding wave functions in the final state.

This seperation of the total wave function into seperate electronic, vibrational and rotational wave functions is the Born-Oppemheimer approximation which is assumed to be a reasonable approximation here. If this approximation is not made, the problem becomes far more complex.

Therefore, the matrix element is proportional to

$$\int \psi_e^* \bar{\mu} \psi_e d\Gamma_e \int \psi_{v'}^* \psi_v d\Gamma_v \int \psi_{J'}^* \psi_j d\Gamma_j$$

Now, the magnetic dipole is almost independent of the internuclear distance and so does not depend upon the vibrational state. Therefore, the orthoganality of the vibrational wave functions shows that the matrix element for the magnetic dipole transition of the type

assumed here is zero within the limitations of the Born-Oppenheimer approximation. Consequently, the magnetic dipole interaction is not considered further.

The quadrupole moment of the molecule, however, depends upon the internuclear distance and may,therefore, cause a transition in which vibrational and rotational states change without any change in the electronic state. It is, therefore, reasonable to investigate the quadrupole interaction.

One more suggestion to look in this direction comes from the calculations of Karl & Poll (1967) in the case of the hydrogen molecule. They calculated the matrix elements $|\langle v'j'|Q|vj\rangle|$ of the quadrupole moment of the H_2 molecule. This was compared with the experimental values of the matrix elements. These experimental values were found from the observed integrated absorption coefficients of various lines in the quadrupole spectrum of H_2. The observations are due to Fink et al. (1965). The experimental and calculated values agree quite well. Some of their values are given below.

Line	Q - Expt.	Q - Calc.	% Discrepancy
S(0)	0.103	0.105	2.0
S(1)	0.0989	0.0969	2.0
S(2)	0.0945	0.0886	6.0
S(3)	0.0833	0.0804	3.5
Q(1)	0.103	0.118	15.
Q(2)	0.112	0.119	6.0
Q(3)	0.111	0.119	6.0

(Transition is from v = 0 to v = 1.)

In the present investigation, the quadrupole moment Q(R) of the O_2 molecule in the ground electronic state is approximated by a cubic expression in $r = R - R_e$, where R is the internuclear distance and R_e is its equilibrium value. Then the matrix elements $\langle vj|Q(R)|v'j'\rangle$ are evaluated for the special case of $v = 0$ and $v' = 1$. This assumes that the vibrational transition is from $v = 0$ to $v' = 1$. This is justified as, at 298°K, the temperature we are considering, more than 99% of the molecules are in the zeroth vibrational level, as calculated from the vibrational partition function. For the evaluation of the above matrix elements, simple harmonic oscillator wave functions are assumed for the vibrational part of the wave function. The total integrated absorption coefficients for the O, S and Q branches, and for the whole band are calculated. The results are discussed in the light of the experimental results of Shapiro and of Bishop.

Pages 13 and 14 are

missing from the original book

CHAPTER II

CALCULATION OF QUADRUPOLE MATRIX ELEMENTS

2.1 FRAMES OF REFERENCE:

In the following we shall refer to two different frames of reference.

i) The laboratory frame of reference O-XYZ, is a frame which is fixed in the laboratory. Along Z-axis of this frame, a plane wave of light is incident. The origin O coincides with the centre of the molecule.

ii) The molecular frame O-xyz is a frame which is fixed w.r.t. the molecule. The internuclear axis lies along z-axis of this frame.

The orientation of O-xyz w.r.t.O-XYZ is specified by Euler angles α,β,γ, as shown in Figure-1.

Three rotations $R_Z(\alpha)$, $R_{y'}(\beta)$ and $R_{z''}(\gamma)$ in this order, take O-XYZ to O-xyz, Oy' and Oz'' are new y- andz-axes after first and second rotations respectively. The usual notation in which $R_u(\theta)$ means a rotation about u-axis, of amount θ is followed.

The co-ordinates of a point in O-XYZ and O-xyz are connected by

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{bmatrix}$$

$$\begin{bmatrix} \cos\gamma & -\sin\gamma & 0 \\ \sin\gamma & \cos\gamma & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \qquad \text{.....2.1}$$

or, $\bar{X} = R\bar{x}$, where

$$R = \begin{bmatrix} \text{Cos}\alpha\text{Cos}\beta\text{Cos}\gamma - \text{Sin}\alpha\text{Sin}\gamma, & -\text{Cos}\alpha\text{Cos}\beta\text{Sin}\gamma - \text{Sin}\alpha\text{Cos}\gamma, & \text{Cos}\alpha\text{Sin}\beta \\ \text{Sin}\alpha\text{Cos}\beta\text{Cos}\gamma + \text{Cos}\alpha\text{Sin}\gamma, & -\text{Sin}\alpha\text{Cos}\beta\text{Sin}\gamma + \text{Cos}\alpha\text{Cos}\gamma, & \text{Sin}\alpha\text{Sin}\beta \\ -\text{Sin}\beta\text{Cos}\gamma & \text{Sin}\beta\text{Sin}\gamma & \text{Cos}\beta \end{bmatrix}$$

.....2.2

The electronic wave function is a function of x, y, z. It is in fact explicitly a function of r_{a_1} , r_{b_1} , θ_{a_1} , θ_{b_1} , ϕ_1 where the meaning of these symbols is given in Figure-2. Among these variables, $\phi$and any two of the r_{a_1} , r_{b_1} , θ_{a_1} , θ_{b_1} are enough to specify the position of the 1st electron, this being true of all the electrons.

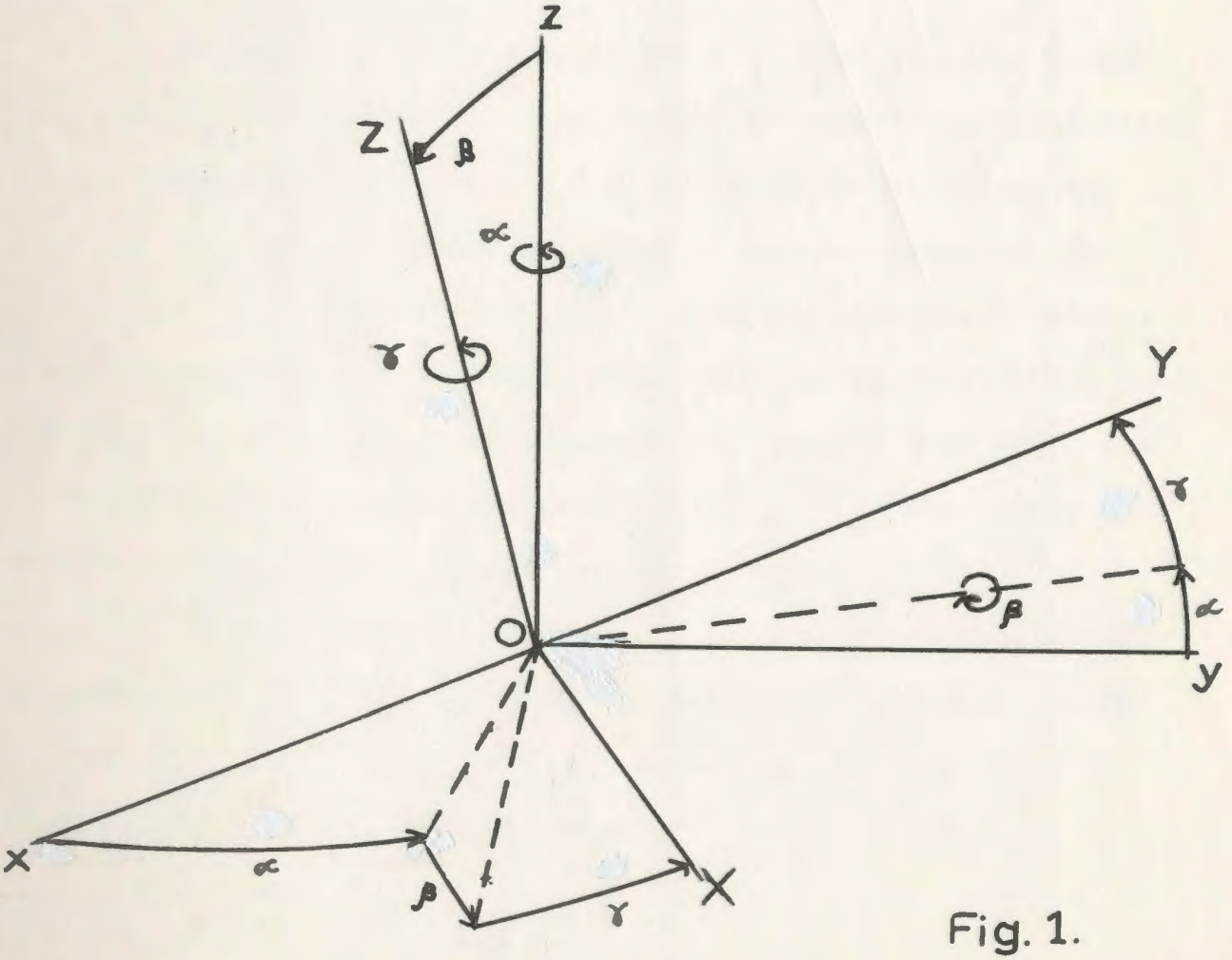
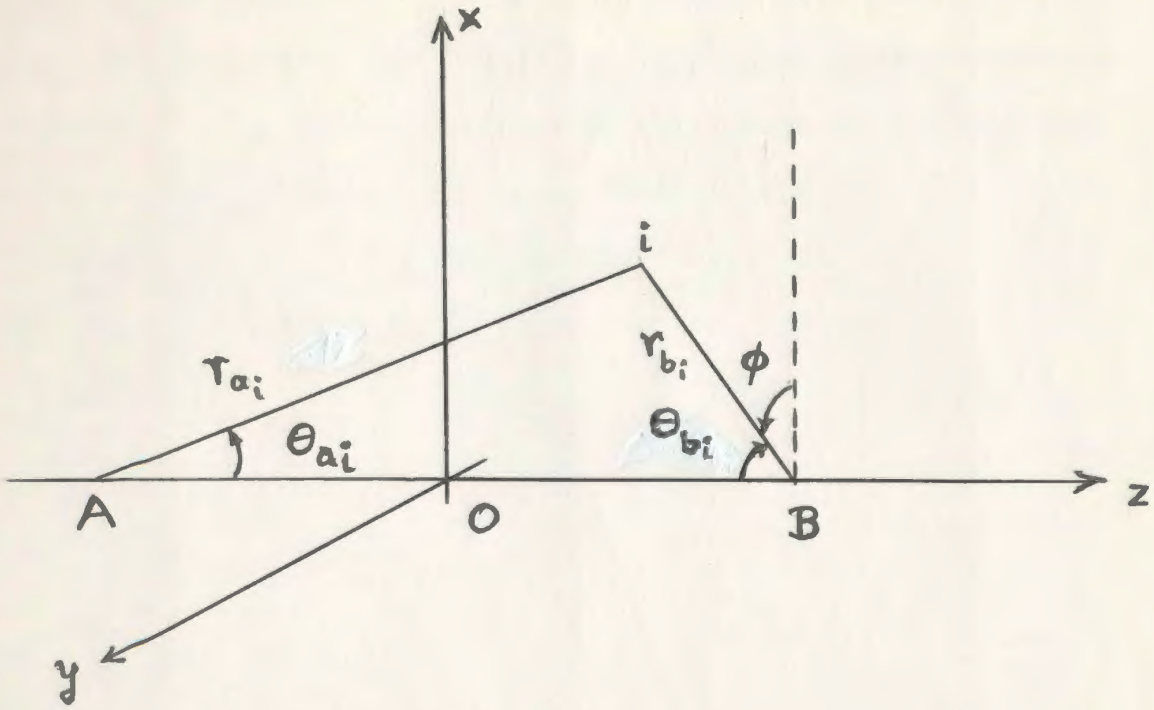


Fig. 1.



2.2 PROBABILITY OF ABSORPTION:

Plane polarized light is assumed to be incident along Z-axis. Photons, comprising this, are in an angular momentum state (ℓ, m) i.e. $\sqrt{\ell(\ell+1)}\, h/2\pi$ is the magnitude of their angular momentum and $mh/2\pi$ is the Z-component of angular momentum. We assume that this plane wave is split into two circularly polarized components. One component, then, contains photons with $m = +1$ and the other contains those with $m = -1$. Photons with $m = 0$ are absent. Therefore, in multipole moments $Q_{\ell m}$, $M_{\ell m}$, etc. terms with $m = +1$ or -1, can only appear.

It is assumed that incident wave is approximately monochromatic and contains frequencies between $\omega - d\omega/2$ to $\omega + d\omega/2$, where ω is the frequency that is absorbed by the molecule in a transition from a state 'i' to state 'f'.

$S(\omega)d\omega$ = No. of photons/cm^2/sec. with frequency between $\omega - d\omega/2$ to $\omega + d\omega/2$. Then the probability per second $P_E(\ell)$ that a molecule absorbs a photon of angular momentum $h/2\pi$ is given by (Blatt and Weiskopf, Theoretical Nuclear physics, 1954,p. 596.)

$$P_E(\ell) = \frac{S(\omega)\, 8\pi^4\, (\ell+1)\,(2\ell+1)\, k^{2\ell-1}}{\left[(2\ell+1)!!\right]^2\, h}\left[\left|Q_{\ell,1} + Q'_{\ell,1}\right|^2 + \left|Q_{\ell,-1} + Q'_{\ell,-1}\right|^2\right] \qquad \ldots\ldots\ldots\ldots 2.3$$

where,

$k = 2\pi\Delta E/h\,c$

$(2\ell+1)!! = (2\ell+1)(2\ell-1)(2\ell-3)\cdots\cdots\cdots 5.3.1.$

and

$$Q_{\ell m} = \sum_n \int e_n r_n^{\ell}\, Y^*_{\ell m}(\theta_n, \phi_n)\, \Phi_f^*\, \Phi_i\, d\Gamma \qquad \ldots\ldots\ldots\ldots 2.4$$

$$Q'_{\ell m} = \frac{-ik}{\ell+1} \sum_n \frac{e_n h}{4\pi M_n c}\, \mu_n \int \dot{r}_n^{\ell}\, \dot{Y}^*_{\ell m}(\theta_n, \phi_n)\, \mathrm{div}\left(\Phi_f^*\, \bar{r}_n \times \bar{\sigma}_n \Phi_i\right) d\Gamma \qquad \ldots\ldots\ldots\ldots 2.5$$

In these expressions,

$Y_{\ell m}$ = spherical harmonic of order ℓ, m,

Φ_i = initial wave function of molecule,

Φ_f = final wave function of molecule,

e_n = charge of the n^{th} particle in the molecular system,

M_n = mass of the n^{th} particle in the molecular system,

c = velocity of light

$\bar{\sigma}_n$ = spin operator of the n^{th} particle in the molecular system,

μ_n = magnetic moment of the n^{th} particle in the molecular system, the summation is over all the particles and integration implies integration over all the space co-ordinates and summation w.r.t. all the spin co-ordinates.

As discussed in Chapter I, we assume that the interaction of the light with the molecule is an electric quadrupole interaction. Hence $\ell = 2$.

Therefore, 2.3, 2.4, 2.5, become

$$P_E(2) = \frac{S(\omega).32\pi^6 \nu^3}{15h} \left[\left| Q_{2,1} + Q'_{2,1} \right|^2 + \left| Q_{2,-1} + Q'_{2,-1} \right|^2 \right] \quad \ldots\ldots\ldots 2.6$$

where $\nu = k/2\pi$ = frequency in wave numbers.

$$Q_{2m} = \sum_n e_n \int r_n^2 \, Y^*_{2m}(\theta_n,\phi_n) \, \Phi^*_f \, \Phi_i \, d\Gamma \quad \ldots\ldots\ldots\ldots 2.7$$

$$Q'_{2m} = -\frac{ik}{3} \sum \frac{e_n h}{4\pi M_n c} \mu_n \int r_n^2 \, Y^*_{2m}(\theta_n,\phi_n) \, \mathrm{div}(\Phi^*_f \bar{r}_n \times \bar{\sigma}_n \Phi_i) d\Gamma \quad \ldots\ldots\ldots\ldots 2.8$$

Now, taking the integrals on the right of the expressions for Q_{2m} and Q'_{2m} to be of the same order, we see that,

$$|Q'_{2m}|/|Q_{2m}| = kh/12\pi Mc \simeq 10^{-6}.$$

We, therefore, neglect Q'_{2m} in comparison to Q_{2m}.

As m = ±1 only,

$$Q_{21} = -e \sum_{n=1}^{16} \int r_n^2 \, Y^*_{21}(\theta_n,\phi_n) \, \Phi^*_f \, \Phi_i \, d\Gamma + 8e \sum_{A,B} \int r_n^2 \, Y^*_{21}(\theta_n,\phi_n) \, \Phi^*_f \, \Phi_i \, d\Gamma$$

and $\ldots\ldots\ldots\ldots 2.7a$

$$Q_{2,-1} = -e \sum_n \int r_n^2 \, Y^*_{21}(\theta_n,\phi_n) \, \Phi^*_f \, \Phi_i \, d\Gamma$$

$$+ 8e \sum_{A,B} \int r_n^2 \; Y_{21}^* (\theta_n, \phi_n) \; \Phi_f^* \; \Phi_i \; d\Gamma \qquad \text{.....2.7b}$$

In these expressions the first term on the right is a summation over sixteen electrons and the second term is a sum over two nuclei A and B.

In the Born-Oppenheimer approximation, Φ the wave function of a molecule is written as

$$\Phi = \Psi_{vj} (R,\Theta,\Phi) \; \Psi_{elect.} \qquad \text{.....2.9}$$

where

$\Psi_{vj} (R,\Theta,\Phi)$ is the wave function of nuclear motion in which, R,Θ,Φ are AB and polar angles of AB.

(This wave function depends on the quantum numbers v, j and m.)

and

$\Psi_{elect.}$ is the wave function of electrons assuming that the nucleii are at rest.

Further,

$$\Psi_{vj} (R,\Theta,\Phi) = Y_{jm} (\Theta,\Phi). \; f_{vj}(R) / R \qquad \text{.....2.10}$$

where $Y_{jm} (\Theta,\Phi)$ are the usual spherical harmonics of order j. The radial wave functions $f_{vj}(R)$ satisfy the equation

$$\frac{d^2 f}{dR^2} + \left[8\pi^2 \mu c \; (E - V(R))/h - j(j+1)/R^2 \right] f = 0. \qquad \text{.....2.11}$$

where V(R) is the average potential of the nuclei in the electric field of the electrons.

We now calculate Q_{21} and $Q_{2,-1}$. First the integration over electronic co-ordinates is carried out. This integral obviously depends upon the internuclear distance R. This is

expressed approximately, as a cubic equation in ($R-R_e$), where R_e is the equilibrium internuclear distance. The successive terms in the equation decrease satisfactorily as seen in Chapter-II Sec.5. The task of expressing this electronic integral as a cubic is straightforward, though quite laborious. After this cubic has been obtained we integrate over the nuclear co-ordinates. The nuclear radial wave functions are in the first approximation, Harmonic Oscillator wave functions and the integration is straightforward. In this way, Q_{21} and $Q_{2,-1}$ can be found. Their determination gives $P_E(2)$ and it can be easily correlated with the integrated absorption coefficient. The integrated absorption coefficients for O, Q, S branches are then calculated. Their sum then gives the total integrated absorption coefficient.

The absorption is assumed to be the one in which the vibrational quantum number v changes from 0 to 1, rotational quantum number j may change by 0 or ±2 and electronic state does not change. It remains in the ground electronic state.

The absorption region, we are interested in,ranges from 1400 cm^{-1} to 1800 cm^{-1}, approximately. Hence, Δv is small. Further, more than 99% of the molecules are in the vibrational state v=0, at T=298^{o}K. Hence we have assumed that v changes from 0 to 1.

The reason for $\Delta j = 0,\pm 2$ is seen explicitly in the expression for the matrix elements calculated. (See page 37). This also follows from the usual selection rules for angular momentum. (Blatt & Weisskopf, Theoretical Nuclear Physics, 1954, p.587.). The assumption that electronic state does not change in

the transition is necessary because spectroscopic transitions between two different electronic states fall usually in the visible or ultraviolet region and not in the infrared region that we are considering here.

2.3 ELECTRONIC WAVE FUNCTION:

Electronic wave function of the O_2 molecule is a solution of

$$H\Psi = E\Psi \qquad \text{.....2.12}$$

where

$$H = -\sum_{i=1}^{16} \left[\frac{h^2}{8\pi^2 m} \nabla_i^2 + \frac{8e^2}{r_{a_i}} + \frac{8e^2}{r_{b_i}} \right] + \sum_{i>j}^{16} \frac{e^2}{r_{ij}} + \frac{64e^2}{R}$$

.....2.13

where

r_{ij} = distance of i^{th} electron from the j^{th} electron.

The terms on the right represent, K.E. of electrons, attractive potential energy in the field of nucleus A, attractive potential enegry in the field of nucleus B, repulsive potential enegry of one electron in the field of other electron, and repulsive potential energy between nucleii, respectively.

The eigen functions of this Hamiltonian can be specified by quantum numbers,

i) Λ specifying component of angular momentum along AB,

ii) I specifying parity,

iii) (for $\Lambda = 0$) v, specifying the charecter of reflection in a plane passing through AB,

iv) S specifying total spin,

v) M specifying component of total spin along AB.

As exact solution of the eigenvalue problem 2.12, is practically impossible, one looks for approximate solutions. The approximate solutions are assumed to be characterized by the same set of quantum numbers given above. Various approximations to the wave function are possible. A great many of them have been studied by Kotani et al (1957) and Meckler (1953). We consider, however, what is usually refered to as antisymmetrized orthogonalized molecular orbital wave function. This is built from linear combination of atomic orbitals. This corresponds to case 1 in Kotani et al. This wave function gives the major contribution to all other approximations, studied by Kotani et al, besides being convenient for numerical calculation.

The two O_2 nuclei are denoted by A and B. The atomic orbitals of atoms A and B are denoted by suffixes 'a' and 'b' respectively. The electronic configuration of the ground state of O_2 atom being $(1s)^2(2s)^2(2p)^4$, atomic orbitals of the type 1s, 2s, 2p are considered. Thus we have five atomic orbitals with suffix 'a' and five with suffix 'b'. They are

$$1s_a(i) = \sqrt{\delta_1^3/\pi}\ \exp(-\delta_1 r_{a_i})$$

$$2s_a(i) = \sqrt{\delta_2^5/3\pi}\ r_{a_i}\ \exp(-\delta_2 r_{a_i})$$

$$2p\sigma_a(i) = \sqrt{\delta_2^5/\pi}\ r_{a_i}\ \exp(-\delta_2 r_{a_i})\ \mathrm{Cos}\theta_{a_i}$$

$$2p\pi_a^+(i) = \sqrt{\delta_2^5/2\pi}\ r_{a_i}\ \exp(-\delta_2 r_{a_i})\ \mathrm{Sin}\theta_{a_i}\ \exp(i\phi_i)$$

$$2p\pi_a^-(i) = \sqrt{\delta_2^5/2\pi}\ r_{a_i}\ \exp(-\delta_2 r_{a_i})\ \mathrm{Sin}\theta_{a_i}\ \exp(-i\phi_i) \qquad \text{.....2.14}$$

and five more with suffix 'b' instead of 'a'.

From the atomic orbitals, unnormalized symmetry orbitals are constructed. They are,

$$
\begin{aligned}
(\sigma 1s)_{g,u} &= 1s_a \pm 1s_b \\
(\sigma 2s)_{g,u} &= 2s_a \pm 2s_b \\
(\sigma 2p)_{g,u} &= 2p\sigma_a \pm 2p\sigma_b \\
(\pi^{\pm}2p)_{g,u} &= 2p\pi^{\pm}_a \mp 2p\pi^{\pm}_b
\end{aligned}
\qquad \ldots\ldots\ldots\ldots\ldots\ldots 2.15
$$

From linear combinations of these, orthogonalized molecular orbitals are constructed, by the Schmidt method (Merzbacher, 1961,p.145). These orthogonalized molecular orbitals are,

$$
\begin{aligned}
\sigma 1_g &= a_{11}(\sigma 1s)_g \\
\sigma 2_g &= a_{21}(\sigma 1s)_g + a_{22}(\sigma 2s)_g \\
\sigma 3_g &= a_{31}(\sigma 1s)_g + a_{32}(\sigma 2s)_g + a_{33}(\sigma 2p)_g \\
\pi^{\pm}_g &= d_g(\pi^{\pm}2p)_g \\
\sigma 1_u &= b_{11}(\sigma 1s)_u \\
\sigma 2_u &= b_{21}(\sigma 1s)_u + b_{22}(\sigma 2s)_u \\
\sigma 3_u &= b_{31}(\sigma 1s)_u + b_{32}(\sigma 2s)_u + b_{33}(\sigma 2p)_u \\
\pi^{\pm}_u &= d_u(\pi^{\pm}2p)_u
\end{aligned}
\qquad \ldots\ldots\ldots\ldots\ldots\ldots 2.16
$$

In these the coefficients a's, b's, and d's are found from the conditions of orthonormality and we have expressed them approximately as cubic equations in $(R-R_e)$, where R is the internuclear distance and R_e is its equilibrium value. The results are given in Table I.

For the calculation of the electronic part we use atomic units i.e. unit of energy = $me^4.4\pi^2/h^2$ and unit of length = $h^2/4\pi^2me^2$

Molecular integrals involving Slater-type atomic orbitals, Eqn. 2.14, are usually expressed in terms of $\alpha_1 = \delta_1 R$ and $\alpha_2 = \delta_2 R$. For α_1, α_2 and we have used the values used by Kotani et. al.(1957).

So that $\alpha_1 = 17.75$, $\alpha_2 = 5.25$ and $R_e = 2.30$ a.u.

The equilibrium internuclear distance of the oxygen molecule in the ground state is known to be 2.282 a.u. So, according to Slater's rule(1930) $\delta_1 = 7.70$ and $\delta_2 = 2.275$, approximately. Our choice of α_1, α_2 and R_e gives, $\delta_1 = 7.7173913$, & $\delta_2 = 2.2826087$. δ_1 and δ_2 are taken to have eight figures and calculations are completed, results being rounded off to the appropriate significant figures at the end. This is done to minimize the truncation error.

We have chosen α_1, α_2 and R_e as above for convenience and for the possibility of comparing our results with those of Kotani et al (1957), wherever possible.

A brief explanation of the construction of completely antisymmetrized wave functions is given in Appendix No. I. The wave function we use, is

$$\Psi = \frac{1}{\sqrt{N!\,2^r}} \sum_P \sum_h U^*_{h1}(P)\, P\Psi_\Omega \cdot \Theta_{s,M,h} \qquad \text{.....2.17}$$

where,

$$\psi_\Omega = \frac{1}{\sqrt{2}} \left[\pi_g^-(1)\pi_g^+(2)\pi_u^-(3,4)\pi_u^+(5,6) - \pi_g^+(1)\pi_g^-(2)\pi_u^+(3,4)\pi_u^-(5,6) \right] \cdot \sigma_{3g}(7,8)\sigma_{2g}(9,10)\sigma_{2u}(11,12)\sigma_{1g}(13,14)\sigma_{1u}(15,16). \qquad \text{.....2.18}$$

In above N is the number of electrons, which is 16 in our case. ' r ' is the number of paired orbitals, which is 7 in the wave function considered. U(P) are the unitary matrices forming an irreducible representation of the permutation group of N electrons (Kotani et al. Table of Molecular Integrals,1955). The summation $\sum_P$ in Eqn. 2.17 is over all the permutations , P, Of N electrons and $\sum_h$ is the sum over a complete set of spin functions $\Theta_{s,M,h}$ belonging

to eigenvalues S and M of total spin and its z-component.

2.4 INTEGRATION OVER ELECTRONIC COORDINATES.

We now carry out the integration, in $Q_{2,1}$ and $Q_{2,-1}$.

$$Q_{2,1} = -e \sum_{n=1}^{16} \int r_n^2 \, Y_{21}^*(\theta_n,\phi_n) \, \Phi_f^* \Phi_i \, d\Gamma \; + \; 8e \sum_{A,B} \int r_n^2 \, Y_{21}^*(\theta_n,\phi_n) \, \Phi_f^* \Phi_i \, d\Gamma$$

As stated before

$$\Phi_i = \Psi_E \, \Psi_{N_i} = \Psi_{3\Sigma_g^-} \, \Psi_{N_i} \, ,$$
$$\Phi_f = \Psi_E \, \Psi_{N_f} = \Psi_{3\Sigma_g^-} \, \Psi_{N_f} \, .$$

Hence,

$$Q_{2,1} = e\sqrt{15/8\pi} \sum_n \int r_n^2 \, \mathrm{Sin}\theta_n \, \mathrm{Cos}\theta_n \, \exp(-i\phi_n) \, \left| \Psi_{3\Sigma_g^-} \right|^2 \Psi_{N_f}^* \, \Psi_{N_i} \, d\Gamma$$

$$-8e\sqrt{15/8\pi} \sum_{A,B} \int r_n^2 \, \mathrm{Sin}\theta_n \, \mathrm{Cos}\theta_n \, \exp(-i\phi_n) \, \left| \Psi_{3\Sigma_g^-} \right|^2 \Psi_{N_f}^* \, \Psi_{N_i} \, d\Gamma$$

Therefore,

$$Q_{2,1} = e\sqrt{15/8\pi} \int_N \left[\int_E \sum_n Z_n (X_n - iY_n) \left| \Psi_{3\Sigma_g} \right|^2 d\Gamma_E \right] \Psi_{N_f}^* \, \Psi_{N_i} \, d\Gamma_N$$

$$-8e\sqrt{15/8\pi} \sum_{A,B} \int_N r_n^2 \, \mathrm{Sin}\theta_n \mathrm{Cos}\theta_n \, \exp(-i\phi_n) \, \Psi_{N_f}^* \, \Psi_{N_i} \, d\Gamma_N \qquad \ldots\ldots\ldots\ldots 2.19$$

The symbol $\int_N d\Gamma_N$ denotes integration over nuclear co-ordinates while $\int_E d\Gamma_E$ denotes integration over electronic co-ordinates.

We will denote the integral over electronic co-ordinates in the first term on the right, by $Q_{21,E}$. Thus

$$Q_{21,E} = \int_E \sum_n Z_n (X_n - iY_n) \left| \Psi_{3\Sigma_g^-} \right|^2 d\Gamma_E \qquad \ldots\ldots\ldots\ldots 2.20$$

In this equation, (X_n, Y_n, Z_n) are the co-Ordinates of the n^{th} electron with respect to O-XYZ. We transform (X,Y,Z) into (x,y,z) by using Eqn. 2.1.

viz:-

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\therefore \quad Z_n(X_n - iY_n) = (R_{31}x_n + R_{32}y_n + R_{33}z_n) \Big[(R_{11} - iR_{21})x_n + (R_{12} - iR_{22})y_n + (R_{13} - iR_{23})z_n \Big]$$

$$= Ax_n^2 + By_n^2 + Cz_n^2 + Fy_nz_n + Gz_nx_n + Hx_ny_n.$$

where

$$A = R_{31}(R_{11} - iR_{21})$$

$$B = R_{32}(R_{12} - iR_{22})$$

$$C = R_{33}(R_{13} - iR_{23})$$

etc. 2.21

Therefore $Q_{21,E}$ becomes

$$Q_{21,E} = AI_{xx} + BI_{yy} + CI_{zz} + FI_{yz} + GI_{zx} + HI_{xy} \quad .....2.22$$

where

$$I_{xx} = \int_E \sum_n x_n^2 \cdot \left| \Psi_{3\Sigma_g^-} \right|^2 d\Gamma_E \quad .....2.23a$$

$$I_{yy} = \int_E \sum_n y_n^2 \cdot \left| \Psi_{3\Sigma_g^-} \right|^2 d\Gamma_E \quad .....2.23b$$

$$I_{zz} = \int_E \sum_n z_n^2 \cdot \left| \Psi_{3_{\Sigma_g^-}} \right|^2 d\Gamma_E \qquad \text{.....2.23c}$$

$$I_{yz} = \int_E \sum_n y_n z_n \cdot \left| \Psi_{3_{\Sigma_g^-}} \right|^2 d\Gamma_E \qquad \text{.....2.23d}$$

etc.

In a similar manner

$$Q_{2,-1} = e\sqrt{15/8\pi} \int_N \left[\int_E \sum_n Z_n (X_n + iY_n) \left| \Psi_{3_{\Sigma_g^-}} \right|^2 d\Gamma_E \right] \Psi^*_{N_f} \Psi_{N_i} d\Gamma_N$$

$$-8e\sqrt{15/8\pi} \sum_{A,B} \int_N r_n^2 \, \mathrm{Sin}\theta_n \mathrm{Cos}\theta_n \exp(+i\phi_n) \, \Psi^*_{N_f} \Psi_{N_i} \, d\Gamma_N$$

.....2.24

Therefore,

$$Q_{2,-1} = Q^*_{2,1} \qquad \text{.....2.25}$$

Now $Q_{2,1,E}$ is calcuiated as a cubic equation in $r = R-R_e$. This is done by calculating I_{xx}, I_{yy} etc. as cubics in r. As stated before this is done by approximating I_{xx}, I_{yy} etc. by cubics in r. As an illustration, we show below how I_{xx} is calculated.

$$I_{xx} = \int_E \Psi^*_{3_{\Sigma_g^-}} \sum_n x_n^2 \cdot \Psi_{3_{\Sigma_g^-}} d\Gamma_E$$

$$= \frac{1}{N!\,2^r} \sum_P \sum_{P'} \sum_h \sum_{h'} U_{h1}(P) \, U^*_{h1}(P') \int_E \Psi^*_\Omega \, T \, P' \Psi_\Omega d\Gamma_E \cdot \Theta_{S,M,h} \cdot \Theta_{S,M,h'}$$

where,

$$T = \sum_n x_n^2 .$$

The matrices U(P) being unitary,

$$U^*_{h1}(P) = U_{1h}(P^{-1}) \ .$$

Therefore,

$$I_{xx} = \frac{1}{N!\,2^r} \sum_P \sum_{P'} \sum_h \sum_{h'} U_{1h'}(P'^{-1})\, U_{h1}(P) \int_E P\Psi_\Omega^*\, TP'\Psi_\Omega d\Gamma_E\, \delta_{hh'}$$

In this, summation over spin variables has given $\delta_{hh'}$. Hence summing over h and h', and changing the variables of integration by transformation,

$$P'x \longrightarrow x \ ,$$

$$I_{xx} = \frac{1}{N!\ 2^r} \sum_{P'} \sum_P U_{11}(P'^{-1}P) \int_E P'^{-1}P\Psi_\Omega\ T\ \Psi_\Omega d\Gamma_E$$

Putting $P'^{-1}P = R,$

$$I_{xx} = \frac{1}{N!\,2^r} \sum_P \sum_R U_{11}(R) \int_E R\Psi_\Omega^*\ T\ \Psi_\Omega d\Gamma_E$$

Thus,

$$I_{xx} = \frac{1}{2^r} \sum_R U_{11}(R) \int_E R\Psi_\Omega^*\ T\ \Psi_\Omega d\Gamma_E$$

But, as seen before, see Eqn.2.18,

$$\Psi_\Omega = \frac{1}{\sqrt{2}} (\Psi_1 - \Psi_2)$$

where

$$\Psi_2^* = \Psi_1 \ .$$

Therefore

$$I_{xx} = \frac{1}{2^{r+1}} \sum_R U_{11}(R) \int_E R(\Psi_1^* - \Psi_2^*)\ T\ (\Psi_1 - \Psi_2) d\Gamma_E$$

$$I_{xx} = \frac{1}{2^{r+1}} \sum_R U_{11}(R) \int_E \left[R\Psi_2 T\Psi_1 + R\Psi_1 T\Psi_2 - R\Psi_1 T\Psi_1 - R\Psi_2 T\Psi_2 \right] d\Gamma_E$$

Further Ψ_1, Ψ_2 are invariant under the permutation Q, where

$Q = (3,4)^{\lambda_1}(5,6)^{\lambda_2}(7,8)^{\lambda_3}.....(15,16)^{\lambda_7}$,

and $\lambda_i = 0$ or 1.

Further any permutation R can be written as

$$R = R_u Q ,$$

where $u = 0,1,2,3,.....,s-1$, and $s = \frac{N!}{2^r}$

Hence

$$I_{xx} = \frac{1}{2^{r+1}} \sum_{R_u} \sum_{Q} U_{11}(R_u Q) \int_E \left[R_u\psi_2 T\psi_1 + R_u\psi_1 T\psi_2 - R_u\psi_1 T\psi_1 - R_u\psi_2 T\psi_2 \right] d\Gamma_E$$

$$= \frac{1}{2^{r+1}} \sum_{R_u} \sum_{Q} \sum_{k} U_{1k}(R_u)\, U_{k1}(Q) \int_E \left[R_u\psi_2 T\psi_1 + R_u\psi_1 T\psi_2 - R_u\psi_1 R\psi_1 - R_u\psi_2 T\psi_2 \right] d\Gamma_E$$

As U(Q) are diagonal matrices and

$$U_{11}(Q) = +1. \qquad \text{(See Appendix No. I)}$$

$$I_{xx} = \frac{1}{2^{r+1}} \sum_{R_u} \sum_{Q} U_{11}(R_u) \int_E \left[R_u\psi_2 T\psi_1 + R_u\psi_1 T\psi_2 - R_u\psi_1 T\psi_1 - R_u\psi_2 T\psi_2 \right] d\Gamma_E$$

Summation over Q gives,

$$I_{xx} = \frac{1}{2} \sum_{R_u} U_{11}(R_u) \int_E \left[R_u\psi_2 T\psi_1 + R_u\psi_1 T\psi_2 - R_u\psi_1 T\psi_1 - R_u\psi_2 T\psi_2 \right] d\Gamma_E \qquad .....2.26$$

Let us now consider the following integrals separately.

$$I = \int R_u\psi_1 T\psi_1 d\Gamma_E$$

$$II = \int R_u\psi_2 T\psi_2 d\Gamma_E$$

$$III = \int R_u\psi_1 T\psi_2 d\Gamma_E$$

and

$$IV = \int R_u \Psi_2 T \Psi_1 d\Gamma_E$$

Consider now I. Note that Ψ_1 and Ψ_2 are of the type,

$\Psi_1 = a(1)b(2)c(3,4)d(5,6)e(7,8)f(9,10)g(11,12)h(13,14)i(15,16)$

$\Psi_2 = b(1)a(2)d(3,4)c(5,6)e(7,8)f(9,10)g(11,12)h(13,14)i(15,16)$

where a, b, c, d.....i are orthonormalized Schmidt orbitals.

We now consider different cases,

Case I : R_u = identity permutation.

$$I = \int a(1)b(2).....i(15,16)\ T\ a(1)b(2).....i(15,16)d\Gamma_E$$

$$= \int a(1)x_1^2 a(1)d\Gamma_1 + \int b(2)x_2^2 b(2)d\Gamma_2 .....$$

$$..... + \int i(16)x_{16}^2\, i(16)d\Gamma_{16}$$

Case II : R_u contains exchange (1,2). Here, because of orthogonality of orbitals

$$I = 0 .$$

Case III : R_u contains exchange (1,s) $s \neq 2$. Here also all terms vanish and we have,

$$I = 0 .$$

Same thing happens in,

Case IV : R_u contains exchange (2,t), $t \neq 1$.

and

Case V : R_u contains exchange (s,t), $s \neq 1, 2$; $t \neq 1, 2$.

Thus

$$I = \sum_{n=1}^{16} \int \Phi_n \, x^2 \, \Phi_n d\Gamma_n$$

where Φ_1, Φ_2, Φ_3.....Φ_{16}, are sixteen orbitals, which are occupied by sixteen electrons.

Now as Ψ_2 has the same form as Ψ_1

$$II = I \ ,$$

while III and IV vanish whatever be R_u. Therefore

$$I_{xx} = -\frac{1}{2} U_{11}(E).2. \sum_{n} \int \Phi_n \, x^2 \, \Phi_n d\Gamma$$

where E = indentity permutation.

Hence,

$$I_{xx} = -\sum_{n} \int \Phi_n \, x_n^2 \, \Phi_n d\Gamma_n \quad .....2.27$$

Similarly

$$I_{yy} = -\sum_{n} \int \Phi_n \, y_n^2 \, \Phi_n d\Gamma_n \quad .....2.28$$

$$I_{zz} = -\sum_{n} \int \Phi_n \, z_n^2 \, \Phi_n d\Gamma_n \quad .....2.29$$

etc.

To calculate $\int \Phi_n \, x^2 \, \Phi_n d\Gamma_n$ etc. the integrals of the type $\int x^2$ (Product of the symmetry orbitals, Eqn.2.15.)$d\Gamma_n$ have to be calculated and to do this integrals of the type $\int x^2$ (Product of Slater type orbitals, Eqn. 2.14)$d\Gamma_n$ have to be evaluated first. All of these are expressed as cubic equations in $r = R - R_e$. The results are given in the next section. Illustrative calculation of $\int \sigma_{1g} \, x^2 \, \sigma_{1g} d\Gamma$ is shown in the Appendix No. II

It is found that $I_{xx} = I_{yy}$, while I_{xy}, I_{yz}, I_{zx} vanish

identically. This follows, in fact, from the rotational symmetry of the molecule about the internuclear axis.

Further if Θ, Φ are the polar angles of AB ie:- of Oz w. r. t. laboratory system O-XYZ, then, in terms of Euler angles,

$$\Theta = \alpha \qquad \text{and} \qquad \Phi = \beta$$

With this, A, B, C, in Eqn. No. 2.22, depend upon Θ, Φ, γ, through their dependence on elements R_{ij} of the rotation matrix R as given by Eqn. No. 2.2. A, B, C can be expressed explicitly as functions of Θ, Φ, γ and the expressions come out as,

$$A = - \sqrt{8\pi/15}\ \mathrm{Cos}^2\gamma\ Y_{2,-1}(\Theta,\Phi) + i\sqrt{8\pi/3}\ \mathrm{Sin}\gamma\ \mathrm{Cos}\gamma\ Y_{1,-1}(\Theta,\Phi)$$

$$B = - \sqrt{8\pi/15}\ \mathrm{Sin}^2\gamma\ Y_{2,-1}(\Theta,\Phi) - i\sqrt{8\pi/3}\ \mathrm{Sin}\gamma\ \mathrm{Cos}\gamma\ Y_{1,-1}(\Theta,\Phi)$$

$$C = + \sqrt{8\pi/15}\ Y_{2,-1}(\Theta,\Phi)$$

.....2.30

Hence $Q_{2,1,E}$ reduces to

$$Q_{2,1,E} = - \sqrt{8\pi/15}\ Y_{2,-1}\ I_{xx} + \sqrt{8\pi/15}\ Y_{2,-1}\ I_{zz}$$

Thus,

$$Q_{2,1,E} = \sqrt{8\pi/15}\ Y_{2,-1}\ (I_{zz} - I_{xx}) \qquad \text{.....2.31a}$$

Consequently,

$$Q_{2,-1,E} = \sqrt{8\pi/15}\ Y^*_{2,-1}\ (I_{zz} - I_{xx}) \qquad \text{.....2.31b}$$

We shall denote

$$I_{zz} - I_{xx} = a_0 + a_1 r + a_2 r^2 + a_3 r^3.$$

The values of the coefficients a_0, a_1, a_2, a_3 will be shown in Table IV. in the next section.

2.5 TABLES:

Here we shall give the results of calculation of some quantities of interest, approximated as cubic equations in r.

Table I

SCHMIDT COEF.	a_0	a_1	a_2	a_3
a_{11}	0.70710592	-0.59193671 x 10^{-5}	-2.0335919 x 10^{-5}	4.6222240 x 10^{-5}
a_{21}	-0.16451502	6.85261 x 10^{-3}	0.202373	1.1105 x 10^{-2}
a_{22}	0.64420459	7.0750313 x 10^{-2}	-1.19132 x 10^{-2}	-8.27689 x 10^{-3}
a_{31}	1.65628 x 10^{-2}	1.24785 x 10^{-2}	-3.0853 x 10^{-2}	2.0001 x 10^{-2}
a_{32}	-0.1565910	-8.988184 x 10^{-2}	-1.561 x 10^{-2}	2.1034 x 10^{-2}
a_{33}	0.6372688	8.652464 x 10^{-3}	4.101 x 10^{-2}	-2.574 x 10^{-2}
b_{11}	0.70710764	-0.59194102 x 10^{-5}	2.0336249 x 10^{-5}	-4.6223600 x 10^{-5}
b_{21}	-0.18141319	2.43669 x 10^{-3}	1.122 x 10^{-2}	-1.2747 x 10^{-2}
b_{22}	0.85443121	-0.16715561	0.10764575	-4.8173 x 10^{-2}
b_{31}	-5.2262825 x 10^{-2}	-4.6694203 x 10^{-2}	2.23 x 10^{-3}	2.496 x 10^{-2}
b_{32}	0.40917139	0.64434128	0.58365	-0.43596
b_{33}	0.94154012	-0.34037130	0.2798	-0.1892
d_g	0.7630578	-8.62629 x 10^{-2}	6.5628 x 10^{-2}	-3.4307 x 10^{-2}
d_u	0.6618967	5.63018 x 10^{-2}	-2.6103 x 10^{-2}	-1.827 x 10^{-3}

Schmidt coefficients are expressed as $a_0 + a_1 r + a_2 r^2 + a_3 r^3$ and a_0, a_1, a_2, a_3 are given in the above table.

Table II

ORBITAL	a_0	a_1	a_2	a_3
$\sigma 1_g$	0.016790448	$-1.3945057 \times 10^{-6}$	2.642989×10^{-6}	$-5.5082819 \times 10^{-6}$
$\sigma 2_g$	0.514558	-1.983×10^{-3}	-8.7803×10^{-3}	-2.0962×10^{-7}
$\sigma 3_g$	0.525544	3.216×10^{-2}	1.493×10^{-2}	-2.483×10^{-2}
π_g^+	0.53300786	4.1652×10^{-2}	-1.4373×10^{-2}	5.215×10^{-4}
$\sigma 1_u$	0.016790190	8.3228532×10^{-7}	2.643008×10^{-6}	5.5084219×10^{-6}
$\sigma 2_u$	0.477220	1.492×10^{-2}	-3.0531×10^{-3}	-2.166×10^{-3}
π_u^+	0.6079670	-1.8588×10^{-2}	-6.991×10^{-3}	9.4002×10^{-3}

$< \phi_n | x^2 | \phi_n >$, where ϕ_n are Schmidt orthonormalized orbitals given by Eqn. No.2.16, are approximated by $a_0 + a_1 r + a_2 r^2 + a_3 r^3$, and the results are given in this table.

Table III

ORBITAL	a_0	a_1	a_2	a_3	
$\sigma 1_g$	1.3392879	1.1499698	0.24991820	7.487094	$\times 10^{-5}$
$\sigma 2_g$	1.5722390	1.1402989	0.371105	5.2	$\times 10^{-3}$
$\sigma 3_g$	1.8730306	1.0621435	0.3158	0.02898	
π_g^+	1.77851	1.03629	0.26293	1.16	$\times 10^{-2}$
$\sigma 1_u$	1.3392927	1.14998534	0.250043	-8.3245633	$\times 10^{-5}$
$\sigma 2_u$	2.26626914	0.8927800	0.29344	-2.26	$\times 10^{-3}$
π_u^+	1.486164	1.187663	0.29576	0.025684	

$< \phi_n | z^2 | \phi_n >$, where ϕ_n are Schmidt orthonormalized orbitals given by Eqn. No. 2.16, are approximated by $a_0 + a_1 r + a_2 r^2 + a_3 r^3$, and the results are given in this table.

Table IV : I_{xx} and I_{zz} are approximated by $a_0 + a_1 r + a_2 r^2 + a_3 r^3$ and the coefficients are given in the following table.

	a_0	a_1	a_2	a_3
I_{xx}	6.601501	0.09930	-0.05053	0.09062
I_{zz}	26.28191	17.61358	4.6695	0.01557

2.6 INTEGRATION OVER NUCLEAR COORDINATES:

We shall now calculate $Q_{2,1}$ and $Q_{2,-1}$ completing the integration over nuclear co-ordinates. We have

$$Q_{2,1} = e\sqrt{15/8\pi} \int Q_{2,1,E}\, \Psi^*_{N_f}\, \Psi_{N_i}\, d\Gamma_N$$

$$- 8e\sqrt{15/8\pi} \sum_{A,B} \int_N r_n^2\, \mathrm{Sin}\theta_n\, \mathrm{Cos}\theta_n\, \exp(-i\phi_n)\, \Psi^*_{N_f}\, \Psi_{N_i}\, d\Gamma_N$$

Using Eqn. No.2.10, 2.31a, and Table IV

$$Q_{2,1} = e \int_N (a_0 + a_1 r + a_2 r^2 + a_3 r^3)\, Y_{2,1}\, \frac{1}{R^2}\, f^*_{v',j'}(R)\, Y^*_{j',m'}(\theta,\phi)\, f_{vj}(R)\, Y_{jm}(\theta,\phi)\, d\Gamma_N$$

$$- 8e \sum_{A,B} \int_N r_n^2\, \mathrm{Sin}\theta_n\, \mathrm{Cos}\theta_n\, \exp(-i\phi_n)\, \frac{1}{R^2}\, f^*_{v',j'}(R)\, f_{vj}(R)\, Y^*_{j',m'}(\theta,\phi)\, Y_{jm}(\theta,\phi)\, d\Gamma_N \cdot \sqrt{15/8\pi}$$

where

$$\Psi_{N_f} = f_{v',j'}(R)\ Y_{j',m'}(\Theta,\Phi)/R \qquad \text{and}$$

$$\Psi_{N_i} = f_{vj}(R)\ Y_{jm}(\Theta,\Phi)/R \qquad \text{have been used.}$$

Noting that the spherical polar co-ordinates of B and A are $(R/2,\Theta,\Phi)$ and $(R/2,\Theta+\pi,\Phi)$ respectively, the second term on the right simplifies, giving,

$$Q_{2,1} = e \int (a_0 + a_1 r + a_2 r^2 + a_3 r^3)\ Y_{2,-1}\ f^*_{v',j'}(R)\ f_{vj}(R)$$
$$Y^*_{j',m'}(\Theta,\Phi)\ Y_{jm}(\Theta,\Phi)\ \mathrm{Sin}\Theta d\Theta d\Phi dR$$
$$- 4e\sqrt{15/8\pi} \int R^2\ \mathrm{Sin}\Theta\ \mathrm{Cos}\Theta\ \exp(-i\Phi)\ f^*_{v',j'}(R)\ f_{vj}(R)$$
$$Y_{j',m'}(\Theta,\Phi)\ Y_{jm}(\Theta,\Phi)\ \mathrm{Sin}\Theta\ d\Theta\ d\Phi\ dR$$

Thus,

$$Q_{2,1} = e \int (a_0 + a_1 r + a_2 r^2 + a_3 r^3 - 4R^2)\ f^*_{v',j'}\ f_{vj}$$
$$Y_{2,-1}\ Y^*_{j',m'}\ Y_{jm}\ \mathrm{Sin}\Theta\ d\Theta\ d\Phi\ dR$$

The integration over angular co-ordinates gives,

$$\int Y_{2,-1}\ Y_{jm}\ Y^*_{j',m'}\ \mathrm{Sin}\Theta\ d\Theta\ d\Phi$$
$$= \left[\frac{5\ (2j+1)}{4\pi\ (2j'+1)} \right]^{1/2} (j,2,0,0|j,2,j',0)\ (j,2,m,-1|j,2,j',m')$$

(See Merzbacher, 1961, p.514.)

where $(j,2,0,0\,|\,j,2,j',0)$ and $(j,2,m,-1|j,2,j',m')$ are usual Clebsch-Gordan coefficients as defined in Merzbacher (1961).

Hence,

$$Q_{2,1} = e \int (a_0 + a_1 r + a_2 r^2 + a_3 r^3 - 4R^2) f^*_{v',j'} f_{vj} \, dR$$

$$\times \left[\frac{5\,(2j+1)}{4\pi(2j'+1)} \right]^{1/2} (j,2,0,0|j,2,j',0)\ (j,2,m,-1|j,2,j',m')$$

We shall denote the integral on the right by $Q_{2,1rad.}$ Therefore,

$$Q_{2,1} = e\, Q_{2,1rad.} \left[\frac{5\,(2j+1)}{4\,(2j'+1)} \right]^{1/2} (j,2,0,0|j,2,j',0) \times$$

$$(j,2,m,-1|j,2,j',m').$$

This is then an expression for $Q_{2,1}$ in the transition

$$^3\Sigma^-_g,\ v,\ j,\ m \longrightarrow {}^3\Sigma^-_g,\ v',\ j',\ m'.$$

We want $|\ Q_{2,1}\ |^2$ for the transition

$$^3\Sigma^-_g,\ v,\ j, \longrightarrow {}^3\Sigma^-_g,\ v',\ j'.$$

where v = 0 and v' = 1. Therefore summing over all possible values of 'm',

$$|\ Q_{2,1}\ |^2 = e^2\ |\ Q_{2,1rad.}\ |^2\ \frac{5\,(2j+1)}{4\pi(2j'+1)}\ |(j,2,0,0|j,2,j',0)|^2$$

$$\sum_m |(j,2,m,-1|j,2,j',m')|^2$$

It can be shown that (See Appendix No. III)

$$\sum_m |(j,2,m,-1|j,2,j',m')|^2 = \frac{(2j'+1)}{5(2j+1)}$$

Therefore,

$$|\ Q_{2,1}\ |^2 = \frac{e^2}{4\pi}\ |\ Q_{2,1rad.}\ |^2\ (j,2,0,0|j,2,j',0)^2$$

.....2.32

Similarly,

$$|Q_{2,-1}\ |^2 = \frac{e^2}{4\pi}\ |Q_{2,-1rad.}\ |^2\ (j,2,0,0|j,2,j',0)^2$$

.....2.33

It is also found that

$$Q_{2,1rad.} = Q_{2,-1rad.}$$

Therefore,

$$| Q_{2,1} |^2 + | Q_{2,-1} |^2 = \frac{e^2}{2\pi} (j,2,0,0|j,2,j',0)^2 | Q_{2,1rad} |^2 \quad \ldots\ldots\ldots\ldots 2.34$$

We shall calculate $Q_{2,1rad.}$ in the next section.

2.7 $Q_{2,1}$ RADIAL:

We have now to calculate

$$Q_{2,1rad.} = \int (a_0 + a_1 r + a_2 r^2 + a_3 r^3 - 4R^2) f^*_{v'j'} f_{vj} \, dR.$$

f_{vj} are in fact the solutions of Eqn. No.2.11. An accurate determination of f_{vj} would need an accurate knowledge of V(R), electronic potential. Knowing V(R) one could solve the Eqn. No. 2.11, either numerically or analytically and get f_{vj}. In the case of H_2 molecule numerical approach has been adopted by Karl and Poll (1967), using the results of Kolos and Wolniewicz (1965). We follow here a simple approach and assume simple harmonic functions as an approximation to f_{vj}. This approximation is good for small v, which is so, in our case. Hence,

$$f_{vj} = N_v \exp(-\alpha r^2/2) H_v(\sqrt{\alpha} r)$$

where

$$r = R - R_e$$

$$\alpha = 2\pi \sqrt{\mu k} / h ,$$

in which

μ = reduced mass of nucleii A, B,

k = force constant of O_2 molecule.

Further

$$N_v = (\alpha/\pi)^{1/4} (2^v v!)^{-1/2}$$

H_v = Hermite polynomial.

Therefore,

$$Q_{2,1rad.} = \int_{-\infty}^{+\infty} (a_0 + a_1 r + a_2 r^2 + a_3 r^3 - 4R^2) N_0 H_0(\sqrt{\alpha} r) N_1 H_1(\sqrt{\alpha} r) \exp(-\alpha r^2) dr$$

The limits of integration should be really form zero to infinity. But as the Harmonic oscillator functions decrease rapidly beyond the classically allowed region, we can extend the lower limit of integration to minus infinity without much error (Pauling and Wilson, 1935, p.269.).

Substituting $x = \sqrt{\alpha} r$

and $4R^2 = 4(r + R_e)^2$

$$= 4R_e^2 + 8R_e r + 4r^2$$

$$Q_{2,1_{rad.}} = N_0 N_1 \int_{-\infty}^{+\infty} (b_0 + b_1/\sqrt{\alpha} .x + b_2/\alpha .x^2 + b_3/\alpha\sqrt{\alpha} .x^3) \cdot H_0(x) H_1(x) \exp(-x^2) dx/\sqrt{\alpha}$$

where,

$$b_0 = a_0 - 4R_e^2$$

$$b_1 = a_1 - 8R_e$$

$$b_2 = a_2 - 4$$

& $b_3 = a_3$

Evaluation of this integral is straightforward. One gets

$$Q_{2,1rad.} = (b_1 + 3b_3/2\alpha)/\sqrt{2\alpha}$$

Using a_1, a_3 from Table No, IV, and R_e=2.3a.u.

we get,

$$b_1 = 35.91428 \text{ a.u.} = 19.00584 \times 10^{-8} \text{ cms.}$$

$$b_3 = -0.07505 \text{ a.u.} = -1.418 \times 10^{7}/\text{cms.}$$

However

$$\alpha = 3.7494 \times 10^{18}/\text{cms}^2$$

Or $\sqrt{\alpha} = 1.9363 \times 10^{9}/\text{cm.}$

$$Q_{2,1\text{rad.}} = 6.941 \times 10^{-17} \left(1 - 2.9852 \times 10^{-5} \right)$$

Hence, neglecting the second term and using Eqn.2.34

$$| Q_{2,1} |^2 + | Q_{2,-1} |^2 = e^2/2\pi (j,2,0,0|j,2,j',0)^2 \times 4.82 \times 10^{-33}$$

Hence, using Eqn. No. 2.6

$$P_E(2) = S(\omega) \frac{32\pi^7\nu^3}{15h} \left[| Q_{2,1} |^2 + | Q_{2,-1} |^2 \right]$$

$$= S(\omega) \frac{16\pi^6\nu^3e^2}{15h} (j,2,0,0|j,2,j',0)^2 \times 4.82 \times 10^{-33}$$

.....2.35

We now connect $P_E(2)$ with integrated absorption coefficient per amagat.

Let I_i = intensity of light before absorption.

I_f = intensity after the absorption, in a path length Δx.

Then

$$I_f = I_i \exp(-k_\nu \Delta x)$$

where k_ν = absorption coefficient.

Therefore $I_i - I_f = I_i k_\nu \Delta x$

$$\int (I_i - I_f) d\nu = I_i \Delta x \int k_\nu d\nu$$

But

$$I_i = S(\omega)d\omega$$

and $$I_f = S(\omega)d\omega - P_E(2)\, N_j \Delta x \rho$$

if N_j = No. of molecules per c.c. at the temperature and pressure considered, in the rotational level j,

ρ = density in amagats.

Therefore,

$$I_i - I_f = P_E(2) N_j \Delta x \cdot \rho$$
$$= S(\omega)\, f(\omega).N_j \Delta x.\rho$$

where we have put

$$P_E(2) = f(\omega)\, S(\omega)$$

Therefore

$$\Delta x \int (I_i - I_f)d\nu = I_i \Delta x \int k_\nu d\nu \qquad \text{gives,}$$

$$\int k_\nu d\nu = \int f(\omega) N_j d\nu/d\omega.\rho$$

But

$$I_{int.} = \text{integrated absorption coefficient} = \int k_\nu d\nu$$

Therefore

$$I_{int.}/\rho = \int f(\omega) N_j d\nu/d\omega$$

$$= \sum f(\omega) N_j / 2\pi c$$

Therefore
$$I_{int.}/\rho = \sum \frac{8\pi^5 \nu^3 e^2}{15hc} \times 4.82 \times 10^{-33}.\ N_j(j,2,0,0|j,2,j',0)^2$$

This comes out to be

$$I_{int.}/\rho = \sum 3.44 \times 10^{-24} N_j \, (j,2,0,0|j,2,j',0)^2$$

.....2.35

The coefficient $(j,2,0,0|j,2,j',0)$ vanishes except when $j' = j-2$, j or $j+2$. This gives absorption coefficients for O, Q and S branches.

We shall calculate the $I_{int.}/\rho$ for various 'j' values for three branches, in the next section. Their sum gives the total integrated absorption coefficient.

CHAPTER III

TOTAL INTEGRATED ABSORPTION COEFFICIENT

3.1 $I_{int.}/\rho$:

In this section we shall calculate $I_{int.}/\rho$ by using Eqn. 2.35

The coefficient $(j,2,0,0|j,2,j',0)$ has non-zero values for $j' = j-2,\ j,\ j+2$ and their squares are given by

$j' = j-2 \qquad (j,2,0,0|j,2,j',0)^2 = 3j(j-1)/2(2j-1)(2j+1)$

$j' = j \qquad (j,2,0,0|j,2,j',0)^2 = j(j+1)/(2j-1)(2j+3)$

$j' = j+2 \qquad (j,2,0,0|j,2,j',0)^2 = 3(j+1)(j+2)/2(2j+1)(2j+3)$

N_j is given by

$$N_j = (2j+1)\, N \exp\left[-B_e j(j+1)hc/kT\right] \div Z$$

T is taken to be $298^{o}K$

and

$$Z = \sum \exp\left[-B_e j(j+1)hc/kT\right](2j+1).$$

Further

$B_e hc/kT = 6.978 \times 10^{-3}$.

As this is small, the sum in Z is replaced by integral from zero to infinity and therefore

$Z = kT/hcB_e = 1.433 \times 10^{2}$ approximately.

But as even-j levels are missing in O_2 molecule, we take

$$Z = \frac{1}{2} \times 1.433 \times 10^{2}$$

Hence, we have

$$N_j = 13.956 \times 10^{-3} \times N\,(2j+1) \exp\left[-j(j+1).\ 6.9782 \times 10^{-3}\right]$$

At T = 298°K. it is sufficient to consider j = 27 as the greatest value of j. This is so because 99.9% of the population of molecules is seen to exist in the levels for which 'j' is less than or equal to 27. Following table gives values of I_{int}/ρ for various values of 'j', for O, Q, S branches.

Total integrated absorption coefficient is then found as the sum of all such absorption coefficients for various branches. The values of $I_{int.}/\rho$ are given in Table No. V on the next page.

Table V

$I_{int.} / \rho$ in $cms.^{-2}$ $amagat^{-1}$ x 10^{-5}

j	O-Branch	Q-Branch	S-Branch
1	0	1.528	0.4585
3	0.2138	0.2217	0.7919
5	0.3492	0.2955	1.015
7	0.4234	0.3321	1.110
9	0.4379	0.3301	1.083
11	0.4040	0.2973	0.9624
13	0.3395	0.2458	0.7879
15	0.2628	0.1881	0.5983
17	0.1888	0.1339	0.4233
19	0.1263	0.08896	0.2799
21	0.0790	0.05534	0.1734
23	0.04626	0.03227	0.1008
25	0.02542	0.01766	0.05499
27	0.01307	0.009052	0.02811
TOTAL	2.9092	3.7761	7.8680

GRAND TOTAL
14.5

CHAPTER IV

DISCUSSION OF RESULTS

The following table gives the values of total intrinsic absorption coefficients as found by Bishop (1966), Shapiro (1965) and the present investigation.

	$I_{int.}/\rho$ cms.$^{-2}$ amagat^{-1}
Bishop	$2.3 \pm 0.9 \times 10^{-3}$
Shapiro	$3.0 \pm 0.23 \times 10^{-4}$
Present	1.45×10^{-4}

Our value is about half of Shapiro's, while Bishop's value is greater than that of Shapiro's by about a factor of 10. Bishop and Shapiro have followed similar methods in finding the $I_{int.}/\rho$. Bishop's experiments were performed with a density of 25 to 80 amagats. The values of $I_{int.}/\rho$ against were plotted and the best straight line found by the least-square method. This intersected $\rho = 0$ axis at 2.3×10^{-3}. Thus the value of $I_{int.}/\rho$ at $\rho = 0$ is found by an extrapolation from the observations made in the region $\rho = 25$ amagats, to $\rho = 80$ amagats. The error bound is the computed standard deviation. The percentage error bound is about 39%. In principle, Shapiro's experiments were conducted along the same lines. The observations were made, however, in the range of $\rho = 5.9$ amagats to $\rho = 12$ amagats. The straight line of $I_{int.}/\rho$ against ρ was obtained by the method of least-squares as in Bishop's experiments. The value 3.0×10^{-4} cms.$^{-2}$amagat^{-1} was found by extrapolation to $\rho = 0$. The error

bound was about 7%. Comparison of error bounds in two cases, and shorter extrapolation in Shapiro's case indicate that Shapiro's results are more trustworthy than Bishop's results. Shapiro has attributed this small $I_{int.}/\rho$ to the presence of water vapour, which is very difficult to remove. Our calculation, which gives a result about half that of Shapiro's, shows that at least half of the effect is due to electric quadrupole interaction, while about half may be due to impurity such as water vapour.

Bishop attributed the intrinsic absorption to the magnetic dipole interaction. Now, O_2 molecule in the ground state has a spin 1 and in fact has a magnetic dipole in its ground state. But as this magnetic dipole is independent of the internuclear distance, it cannot cause a transition, which we have considered. Such a transition is ruled out by the ortogonality of vibrational states with v = 0 and v = 1. The present calculation, however, shows that most of the value of $I_{int.}/\rho$ at $\rho = 0$ found by Bishop appears to be due to impurity or experimental error, such as large extrapolation.

We have neglected higher multipole interactions. To consider its effect

$$Q_{l,m} = \sum e \int r^{l} Y^{*}_{l,m} \Phi^{*}_{f} \Phi_{i} d\Gamma$$

$$= e_t r^{l} \quad \text{approximately.}$$

where

r = linear dimensions of molecule

e_t = total electronic charge.

Therefore

$$\frac{|Q_{3,1}|}{|Q_{2,1}|} = e_t r^3 / e_t r^2 = r = 10^{-8}$$

Thus, the octopole absorption probability is $k^2 .10^{-16}$ times smaller than that in the quadrupole case i.e. at least 10^{-6} times smaller. Hence, neglecting higher multipoles would not cause an error greater than 10^{-4}%. We have also neglected the term in r^3 in the calculation of $Q_{2,1rad.}$. We have seen that this introduces an error of about $3 \times 10^{-5} \times Q_{2,1rad.}$ in $Q_{2,1rad.}$. Therefore, in the $I_{int.}/\rho$ it introduces an error of about $6 \times 10^{-5}.I_{int.}/\rho$ i.e. 6×10^{-3}% approximately. Both of these errors being quite small, the improvement in our calculation does not appear to be in the direction of higher multipole interactions or allowing terms higher than r^3 in our expansion of $Q_{2,1Elec.}$ We must, therefore, take a better electronic function for the ground state. Kotani et al(1957) have studied various approximations to the ground state electronic wave function of O_2 molecule. Their best wave function lowers the energy by about 10%. It is hoped that, that will similarly improve derivative of Q. We can qualitatively see it this way. Lowering of energy implies greater overlap of electron clouds, round A and B. This will increase charge density in the overlap region, which in turn may increase Q'.

In our calculation, we have calculated $< x^2 >$ and $< z^2 >$ in the ground electronic state. We have calculated these quantities by expressing all the molecular integrals involved, approximately, as cubic equations in r. Throughout the caculation, we have

retained eight figures and have rounded off to three figures, at the end. This is done to minimize the truncation error. Kotani et al (1957) have also calculated these quantities at equilibrium internuclear distance. If we put r = 0 in the expression for $\langle x^2 \rangle$ and $\langle z^2 \rangle$ we get the values for the equilibrium internuclear distance. Our values of $\langle x^2 \rangle$ and $\langle z^2 \rangle$ are higher than Kotani's values by about 8% and 3% respectively. This maybe due to some kind of truncation effect in Kotani's calculations. We do not know the numerical details of their calculation. Our δ_1 is greater than their's by 0.004% and δ_2 is greater by 0.01%. To see if this causes a great perturbation, we calculated $\langle x^2 \rangle$ and $\langle z^2 \rangle$ at r = 0 taking Kotani's δ_1 and δ_2 and carrying over 8 figures throughout. This changed the values of $\langle x^2 \rangle$ and $\langle z^2 \rangle$ at r = 0 by only 0.02%.

Though still lower density experiments on the line of Shapiro's work, which would reduce the error due to extrapolation still more, would give a better experimental result for comparison, the comparison of the order of magnitude of Shapiro's and our values of $I_{int.}/\rho$, shows that, part of the effect is surely due to electric quadrupole interaction.

APPENDIX I

ELECTRONIC WAVE FUNCTION

A 1.1 SPIN FUNCTIONS OF SINGLE ELECTRON:

Spin functions $\theta(\sigma)$ of the z-component of spin measured in units of $h/2\pi$ belong to eigenvalues +1/2 & -1/2. Thus

$$\sigma = +1/2 \text{ or } -1/2.$$

As σ takes on two values, there are two linearly independent spin functions α and β such that,

$$\alpha(1/2) = 1 \qquad \beta(1/2) = 0$$

$$\alpha(-1/2) = 0 \qquad \beta(-1/2) = 1.$$

These satisfy,

$$\int |\alpha(\sigma)|^2 d\sigma = \int |\beta(\sigma)|^2 d\sigma = 1 ,$$

$$\int \alpha^*(\sigma)\, \beta(\sigma) d\sigma = 0 \qquad \text{.....A1.1}$$

Further, if

$$s_+ = s_x + i s_y$$

$$s_- = s_x - i s_y ,$$

where s_x, s_y are x- and y- components of the spin $\bar{s}$, then

$$s_+\alpha = 0 \qquad s_-\alpha = \beta \qquad s_z\alpha = \frac{1}{2}\alpha$$

$$s_+\beta = \alpha \qquad s_-\beta = 0 \qquad s_z\beta = -\frac{1}{2}\beta$$

.....A1.2

From these relations one can show that,

$$s^2\theta = s(s+1)\theta \qquad \text{where} \quad s = \frac{1}{2}$$

and $\theta = \alpha$ or β.

A 1.2 SPIN FUNCTIONS OF 'N' ELECTRONS :

In the space of spin functions of 'N' electrons, we have 2^N linearly independent spin functions,

$$\theta_1(\sigma_1)\theta_2(\sigma_2) \ldots\ldots\ldots\ldots\ldots\theta_N(\sigma_N)$$

where

$$\theta_i = \alpha \text{ or } \beta$$

$$i = 1, 2, 3, \ldots\ldots\ldots\ldots\ldots\ldots N.$$

We will denote eigenfunctions of S^2 and S_z by $\Theta_{S,M}$. Here S^2 denotes the square of the total spin operator and S_z is its z-component.

viz.: $\bar{S} = \bar{s}_1 + \bar{s}_2 + \bar{s}_3 + \ldots\ldots\ldots\ldots\ldots + \bar{s}_N$

and $S_z = s_{1z} + s_{2z} + s_{3z} + \ldots\ldots\ldots\ldots\ldots + s_{Nz}$.

The suffixes 'S' and 'M' of $\Theta_{S,M}$ are quantum numbers of total spin and its z-component.

e.g.: $\alpha\cdot\alpha\cdot\alpha\cdot\alpha\ldots\ldots\ldots\ldots\ldots = \Theta_{N/2,N/2}$

Now $\Theta_{N/2,M}$ for M = N/2 - 1, N/2 - 2, ;....., - N/2. can be obtained from $\Theta_{N/2,N/2}$ by a repeated application of S_-, using usual result,

$$S_-\Theta_{S,M} = \sqrt{(S + M)(S - M + 1)}\ \Theta_{S,M-1}.$$

.....A1.3

Now the subspace for which M = N/2 - 1, is N dimensional. In this subspace one of the functions is $\Theta_{N/2,N/2-1,}$. Hence there still exist (N - 1) more linearly independent functions. These functions must belong to S = N/2 - 1. We can choose any set of (N - 1) orthonormal functions $\Theta_{N/2 - 1,N/2 - 1;k}$ (k = 1, 2, ...N-1.) which are orthogonal to $\Theta_{N/2,N/2 -1}$, as basis of (N - 1) dimensional subspace of functions for which S = N/2 - 1, M = N/2 - 1.

Similarly, in N(N-1)/2 dimensional subspace of M = (N/2 - 2)we have already N functions

$$\Theta_{N/2,N/2-2}\ ,\qquad \Theta_{N/2-1,N/2-2,k}$$

There can still be

$$N(N-1)/2 - N = N(N-3)/2$$

functions

$$\Theta_{N/2-2,N/2-2,k} \qquad k = 1,2,3,.....N(N-3)/2$$

which are mutually orthogonal and are also orthogonal to N functions

$$\Theta_{N/2,N/2-2}\ ,\qquad \Theta_{N/2-1,N/2-2,k}$$

$$k = 1,2,3,.....N-1.$$

Continuing this way, we can construct 2^N linearly independent functions, which span the space of N electrons. Further, each of these is an eigenfunction of S^2 and S_z belonging to the eigen values S(S + 1) and M respectively.

If there are $f^N_{S,M}$ l.i. eigenfunctions of S^2 and S_z belonging to eigen values S(S +1) and M, then

f^N_S = difference in dimensions of spin-function spaces for which M = S and M = S + 1.

Therefore,

$$f^M_S = C^N_{N/2+S} - C^N_{N/2+S+1} = \frac{(2S+1)\,N!}{(N/2+S+1)!\;(N/2-S)!} \qquad .....A\ 1.4$$

A 1.3 PERMUTATIONS AND REPRESENTATION MATRICES:

Consider any permutation P of N electrons. There can be N! different permutations, which form a group called symmetric group. We shall denote this by G_N. In this connection we have the

following theorem.

Theorem:

We can express $P\Theta_{S,M,k}$ linearly in terms of f_S^N functions $\Theta_{S,M,h}$ $h = 1,2,3.....f_S^N$.

viz. $$P\Theta_{S,M,k} = \sum_h V_{hk}(P)\Theta_{S,M,h} \qquad .....A\ 1.5$$

Proof:

We note that P commutes with S^2 and S_z. Therefore, $P\Theta_{S,M,k}$ is an eigenfunction of S^2 and S_z belonging to the eigen values $S(S+1)$ and M, respectively. So, $P\Theta_{S,M,k}$ belongs to the f_S^N dimensional spin-space of N electrons, in which $\Theta_{S,M,h}$ are basis functions. Hence, $P\Theta_{S,M,k}$ must be expressible as linear combination of basis functions.

Hence the theorem.

$V_{hk}(P)$ form a matrix, which is a representation of permutation group G_N. This representation is irreducible.

A 1.4 EXPANSION OF ANTISYMMETRIC WAVEFUNCTION:

Consider $\Phi(\bar{r}_1,\sigma_1,\bar{r}_2,\sigma_2,.....\bar{r}_N,\sigma_N)$ to be an eigenfunction of Hamiltonian H, of N electron system. This function must be antisymmetric w.r.t. simultaneous permutations of position and spin varibles of electrons.

We assume that H is spin-free. Therefore, H, S^2 and S_z commute with each other. Hence $\Phi_{S,M}$ can be chosen so that,

$$S_-\Phi_{S,M} = \sqrt{(S+M)(S-M+1)}\,\Phi_{S,M-1}$$

But $\Theta_{S,M,k}$ $\quad k = 1,2,3.....f_S^N$

$M = S, S-1,..... -S$

$S = N/2, N/2-1.....-N/2$

form a complete set in the spin-space of N electrons. Hence, any antisymmetric function can be expressed in terms of Θ's linearly Therefore,

$$\Phi_{S,M}(\bar{r}_1,\sigma_1,\bar{r}_2,\sigma_2\ldots\ldots\ldots) = \frac{1}{\sqrt{f_S^N}} \sum_k \Psi_{S,k}(\bar{r}_1,\bar{r}_2,\bar{r}_3\ldots\ldots)\,\Theta_{S,M,k}(\sigma_1,\sigma_2\ldots\ldots) \qquad \ldots\ldots\ldots\ldots\ldots\text{A1.6}$$

The coefficients $\Psi_{S,k}$ are the same for (2S + 1) functions $\Phi_{S,M}$ (M = S,S - 1,S - 2..... -S) because $\Phi_{S,M}$ and $\Theta_{S,M,k}$ must undergo the same transformation by operation S_- . Thus, if

$$e_P = +1 \quad \text{if P = even permutation}$$
$$= -1 \quad \text{if P = odd permutation,}$$

then,

$$e_P\,\Phi_{S,M} = \frac{1}{\sqrt{f_S^N}} \sum_k P\Psi_{S,k} \cdot P\Theta_{S,M,k} \,. \qquad \ldots\ldots\ldots\ldots\ldots\text{A1.7}$$

Using equation A 1.5

$$\Phi_{S,M} = \frac{e_P}{\sqrt{f_S^N}} \sum_k P\Psi_{S,k} \sum_h V_{hk}(P)\Theta_{S,M,h}$$

Comparing this with A 1.6, we get

$$\Psi_{S,h} = e_P \sum_k V_{hk}(P) P\,\Psi_{S,k} \qquad \ldots\ldots\ldots\ldots\ldots\text{A1.8}$$

Multiplying this by $V_{kh}(P^{-1})$ and summing over h gives,

$$P\,\Psi_{S,k} = e_P \sum_h V_{kh}(P^{-1})\,\Psi_{S,h}$$

we now put

$$U(P) = e_P\, V(P^{-1})^{\dagger} \qquad \ldots\ldots\ldots\ldots\ldots\text{A1.9}$$

where,

† denotes transposition of a matrix.

Thus,

$$P\ \Psi_{S,k} = \sum_h U_{hk}(P)\ \Psi_{S,h} \qquad \text{.....A1.10}$$

The matrices U(P) also form an irreducible representation of G_N . Eqn. A1.10 is the condition that $\Psi_{S,k}$ have to satisfy so that when multiplied by spin functions and summing they give an antisymmetrized function $\Phi_{S,M}$.

We shall denote representation V(P) by D_S^N and representation U(P) by $\bar{D}_S^N$ .Note that in Eqn. A1.6 if Φ is totally antisymmetrized, then, $\Psi_{S,k}$ and $\Theta_{S,M}$ form bases of representations $\bar{D}_S$ and D_S respectively.

A 1.5 CONSTRUCTION OF BASES OF $\bar{D}_S$:

In constructing completely antisymmetrized wavefunction of N electrons, we generally start with a " primitive function "

$$\Psi^o(\bar{r}_1,\bar{r}_2,\bar{r}_3 \ldots\ldots\ldots \bar{r}_N) \qquad \text{.....A1.11}$$

This function is not yet symmetrized. In individual electron approximation, one takes

$$\Psi^o = \Psi_1(\bar{r}_1)\ \Psi_2(\bar{r}_2)\ldots\ldots\ldots\Psi_N(\bar{r}_N) \qquad \text{.....A1.12}$$

In the case we have considered

$$\Psi^o = \Psi_a(\bar{r}_1,\bar{r}_2)\Psi_b(\bar{r}_3,\bar{r}_4)\ldots\ldots\ldots\text{etc.} \qquad \text{.....A1.13}$$

where

$$\Psi_a(\bar{r}_1,\bar{r}_2) = \Psi_a(\bar{r}_2,\bar{r}_1)$$

Now, by applying all permutations to Ψ^o we obtain N! functions $P\Psi^o$. These functions maybe linearly dependent or inde-

pendent, depending upon the symmetry properties of function . In the case described by Eqn. A1.11, $P\psi^o$ are linearly independent. In the case of Eqn. A 1.13, this is not so. We shall first consider the case wherein $P\psi^o$ are linearly independent.

By forming linear combinations of $N!$ functions $P\psi^o$, we want to find a set of functions, which are bases of $\bar{D}_S$. This can be done in the following manner.

Let $U_{kh}(P)$ be $(k,h)^{th}$ element of matrix for the permutation P in the irreducible representation $\bar{D}_S$ of G_N . Then, we have usual ortogonality relation

$$f_S/N! \sum_P U^*_{km}(P)U_{hn}(P) = \delta_{mn}\delta_{kh} \qquad \text{.....A1.14}$$

(Kotani et al,Table of Molecular Integrals,1955)

This shows that $N!$ dimensional matrix

$$| T_{km,P} | = | \sqrt{f_S/N!}\, U^*_{km}(P) | ,$$

whose rows are numbered by (km) and whose columns are numbered by permutation P, is unitary.

Consider now transform of $N!$ functions $P\psi^o$ by matrix T.

i. e. $$\psi_{km} = \sqrt{f_S/N!} \sum_P U^*_{km}(P)P\psi^o \qquad \text{.....A1.15}$$

As this is a unitary transformation, ψ_{km} are linearly independent if $P\psi^o$ are.

$$P\,\psi_{km} = \sqrt{f_S/N!} \sum_R U^*_{km}(R)PR\psi^o$$

$$= \sqrt{f_S/N!} \sum_R U^*_{km}(P^{-1}R)R\psi^o$$

$$= \sqrt{f_S/N!} \sum_R \sum_h U^*_{kh}(P^{-1})U^*_{hm}(R)R\psi^o$$

$$= \sum_h U_{hk}(P)\ \Psi_{hm}$$

Thus Ψ_{km} do form a basis for the representation $\bar{D}_S$. Now, if the representation $\bar{D}_S$ is dual to D_S for a definite value of S, then

$$\Psi_{km} = \Psi_{S,km} \qquad k = 1,2,3,4.....f_S^N$$

have the desired transformation property Eqn. A1.10. For m = 1,2, 3.....f_S^N we have f_S^N independent sets of such functions. Hence, we have the same number of antisymmetric functions.

$$\Phi^m_{S,M} = 1/\sqrt{f_S} \sum_k \Psi^m_{S,k}\ \Theta_{S,M,k}$$

$$= 1/\sqrt{N!} \sum_P \sum_k U^*_{km}(P) P\Psi^o \cdot \Theta_{S,M,k} \qquad .....A1.16$$

Let us consider the case, in which $\Psi^o(\bar{r}_1,\bar{r}_2, \bar{r}_3.....$ $...\bar{r}_N)$ is symmetric w.r.t. the exchanges of two electrons in r pairs (1,2) (3,4).....(2r - 1, 2r). This is the case of our interest.

Let h be the subgroup of G_N, consisting of 2^r elements

$$Q = (1,2)^{\lambda 1}\ (3,4)^{\lambda 2}\ .....(2r - 1,2r)^{\lambda_r} \qquad .....A1.17$$

λ_i = 0 or +1

i = 1,2,3.....r.

Then

$$Q\Psi^o = \Psi^o \qquad \text{for any Q belonging to h.}$$

Let us select $s = N!/2^r$ elements $P_0,P_1,P_2.....P_{s-1}$ out of factorial N! elements of G_N in such a manner that $P_i^{-1}P_j$ does not belong to h for any pair P_i,P_j . Then, any element P of G_N can be uniquely expressed as

$$P = P_u Q$$

Thus

$$P\Psi^o = P_u Q\Psi^o = P_u\Psi^o$$

Hence we have, at the most, 's' linearly independent functions among $N_!$ functions $P\Psi^o$. We assume that these 's' functions

$$P_u\Psi^o, \qquad u = 0,1,2.....s-1$$

are linearly independent.

Now, Q's are commutative and $Q^2 = E$. Hence, all the irreducible representations of h are one dimensional and the matrices of representatinn are either +1 or -1. We can take matrices of representation $\bar{D}_S$ in such a manner that matrices of elements of h appear in the reduced form. With this,

$$U_{kh}(Q) = \pm\delta_{kh} \quad \text{for all Q in h.}$$

Further, we number the rows and columns of these matrices in such a way that the first 'g' diagonal elements are +1 for all 2^r matrices U(Q):

$$U_{kk}(Q) = +1 \qquad 1 \leq k \leq g, Q \text{ in h.}$$

while other diagonal elements $U_{kk}(Q)$ take value -1 for atleast one of the elements Q. With this choice of U(Q)'s one can prove that the first 'g' mambers of $\Phi^m_{S,k}$ (m = 1,2,3.....) are linearly independent, while the rest of them vanish identically (Kotani, Table of Molecular Integrals, 1955).

Further, if s functions $P_0\Psi^o, P_1\Psi^o.....P_{s-1}\Psi^o$ are orthogonal, then g functions

$$\Phi^m = 1/\sqrt{N_! \, 2^r} \sum_P \sum_k U^*_{km}(P) P\Psi^o \cdot \Theta_{S,M,k} \qquad .....A1.18$$

$$m = 1,2..... g.$$

are orthonormal. Thus these functions form an orthonormal set and each of the m is antisymmetrized.

A 1.6 SPIN FUNCTIONS $\Theta_{S,M,h}$:

If Ψ^o is invariant under the exchanges belonging to h then $\Theta_{S,M,m}$ for $m \leq g$ must change sign under the same exchange. Hence, the spin functions of the first 'g' members must be of the form,

$$\prod_{t=1}^{r} \frac{\alpha_{2t-1}\beta_{2t} - \beta_{2t-1}\alpha_{2t}}{\sqrt{2}} \quad \Theta'_{S,M,h}(2r+1, 2r+2 \ldots\ldots N)$$

$$h = 1,2,3.\ldots\ldots\ldots\ldots g.$$

The first 'r' factors contribute nothing to the total spin. Thus,

$$\bar{S} = \bar{S}' = \bar{S}_{2r+1} + \bar{S}_{2r+2} + \ldots\ldots\ldots\ldots + \bar{S}_N$$

Hence Θ' must be an eigenfunction of $\bar{S}'^2$ and S'_z .

For the case, which we have considered in the calculation

$$\Theta' = 1/\sqrt{2}\ \alpha(1)\alpha(2)\left[\alpha(3)\beta(4) - \beta(3)\alpha(4)\right]$$

A 1.7 CONSTRUCTION OF WAVEFUNCTIONS OF PROPER SYMMETRY:

The symmetric character of the wavefunctions is specified, in our solution, by quantum numbers Λ,I,v,S and M (See pg. 14). The set Λ,I,v shall be abbreviated by Ω.

We have constructed ten Schmidt orbitals Eqn. No. 2.16. We select all the possible sets of sixteen orbitals, whose products have the given symmetry (Λ,I), considering that each orbital can accomodate at the most two electrons. For a particular set , then, we make a product function of these sixteen orbitals. As 16 electrons are assigned to 10 Schmidt orbitals, each of which can

accomodate at the most two electrons, the number of orbitals which contain only one electron is at the most four, Thus, there will be few paired orbitals and two or four unpaired ones. In writing the product, we have written first, unpaired and then, paired orbitals. We then multiply the product function by a spin function of desired symmetry S,M and antisymmetrize the result to get the wavefunction of proper symmetry, Λ,I,S,M.

For $\Lambda = 0$, the required wavefunction is found by taking the real part for $\sum^{+}$ and imaginary part for $\sum^{-}$, of the product function and doing the same thing as before, we get the wavefunction of proper symmetry Ω,S,M. This can be done for each set.

APPENDIX II

$< \sigma 1_g | x^2 | \sigma 1_g >$ AN ILLUSTRATATIVE CALCULATION

We show here how $< \sigma 1_g | x^2 | \sigma 1_g >$ is approximated by a cubic equation in 'r'.

$$< \sigma 1_g | x^2 | \sigma 1_g > = \int (\sigma 1_g)^2 \, x^2 d\Gamma$$

$$= a_{11}^2 \int (\sigma 1s_g)^2 x^2 d\Gamma$$

$$= a_{11}^2 \int (1s_a + 1s_b)^2 \, x^2 \, d$$

$$= 2a_{11}^2 \left[\int (1s_a)^2 \, x^2 \, d\Gamma + \int (1s_a)(1s_b) \, x^2 \, d\Gamma \right]$$

$$= 2a_{11}^2 \left[1/\delta_1^2 + \alpha_1^3 \, R^2 \, (\, 5A_4 - 6A_2 + A_0 \,)/120 \right]$$

.....A2.1

where

$$A_n = A_n(\alpha_1) = \int_1^\infty \exp(-\alpha\lambda) \, \lambda^n d\lambda$$

Now

$$\alpha_1^3 R^2 = \delta_1^3 \, R^5$$

$$\alpha_1^3 R^2 = \delta_1^3 (r + R_e)^5 \qquad \text{.....A2.2}$$

Further,

$$A_n(\alpha_1) = A_n(\delta_1 R)$$

$$= A_n(\delta_1 r + \delta_1 R_e)$$

$$= A_n(x_0 + x)$$

where

$$x_0 = \delta_1 R_e \qquad \text{and} \qquad x = \delta_1 r$$

hence using Taylor's expansion

$$A_n(x_0 + x) = A_n(x_0) + x\,A_n'(x_0) + \frac{x^2}{2} A_n''(x_0) + \frac{x^3}{6} A_n'''(x_0)$$

neglecting x^4 etc.

In this primes denote the differentiation w.r.t. x.

But

$$A_n(\alpha) = \int_1^\infty \exp(-\alpha\lambda)\ \lambda^n\ d\lambda$$

Hence differentiating w.r.t. α

$$A_n'(\alpha) = -A_{n+1}(\alpha).$$

Therefore

$$A_n(x_0 + x) = A_n(x_0) - x\,A_{n+1}(x_0) + \frac{x^2}{2} A_{n+2}(x_0) - \frac{x^3}{6} A_{n+3}(x_0)$$

approximately.

Or

$$A(\alpha_1) = A_n - \delta_1 r\,A_{n+1} + \frac{\delta_1 r^2}{2} A_{n+2} - \frac{\delta_1 r^3}{6} A_{n+3}$$

.....A2.3

In this equation A_n's are functions of $\delta_1 R_e$.

Using Eqn. No. A2.1, A2.2, and A2.3 one can easily approximate $\langle \sigma 1_g | x^2 | \sigma 1_g \rangle$ by a cubic equation in 'r'.

APPENDIX III

DERIVATION OF A RESULT

The coefficients satisfy the orthogonality relation

$$\sum_{m_1,m}(j_1,j_2,m_1,m_2|j_1,j_2,j,m)\ (j_1,j_2',m_1,m_2'|j_1,j_2',j,m) = \frac{2j+1}{2j_2'+1}\,\delta_{j_2j_2'}\delta_{m_2m_2'}$$

(See A.S. Devydov,1965,p.147)

Hence,

$$\sum_{m',m}(j,2,m,-1|j,2,j',m')^2 = \frac{2j'+1}{5}$$

But

$$m' = m - 1.$$

Therefore summation over m' is the same as summation over m. Hence

$$\sum_{m}\sum_{m}(j,2,m,-1\ j,2,j',m')^2 = \frac{2j'+1}{5}$$

Let

$$\sum_{m}(j,2,m,-1\ j,2,j',m') = f.$$

Then 'f' does not depend upon 'm'. Thus,

$$\sum_{m} f = \frac{2j'+1}{5}$$

Or

$$f\ (2j+1) = \frac{2j'+1}{5}$$

Hence,

$$\sum_{m}(j,2,m,-1|j,2,j',m')^2 = \frac{2j'+1}{5(2j+1)}\ .$$

BIBLIOGRAPHY

1. Bishop R. B. 1966, M.Sc. Thesis, Memorial University of Newfoundland, St.Johns, NEWFOUNDLAND.

2. Shapiro M. M. 1965, Ph.D. Thesis, The University of Toronto, Toronto, ONT.

3. Herzberg G. 1965, Spectra of Diatomic Molecules, D. Van Nostrand Co.,Inc.

4. Karl G. and Poll J. D. 1967, J. Chem. Phys. 46, 2944.

5. Fink U., Wiggins T.A. and Rank D. H. 1965, J. Mol. Spectry. 18, 384.

6. Blatt J. M. and Weisskopf V. F. 1954, Theoretical Nuclear Physics, John Wiley & Sons,N.Y.

7. Kotani M., Mizuno Y.,and Kayama K. 1957, J. Phy. Soc. of Japan, 12, 707.

8. Meckler A. 1953, J. Chem. Phys. 21, 1750.

9. Merzbacher E. 1961, Quantum Mechanics, John Wiley & Sons, Inc. N.Y.

10. Slater J. 1930, Phys. Review, 36, 57.

11. Kotani M., Amemiya A., Ishiguro E. & Kimura T. 1955, Table of Molecular Integrals, Maruzen Co., Ltd., Tokyo.

12. Kolos W. and Wolniewicz L. 1965, J. Chem. Phys. 43, 2429.

13. Pauling L. and Wilson E. B. 1935, Introduction to Quantum Mechanics, McGraw-Hill Book Co., Inc. N.Y.

14. Davydov A. S. 1965, Quantum Mechanics, Addison-Wesley Publishing Co. Inc.

ACKNOWLEDGEMENTS

The author wishes to acknowledge his debt of gratitude to Dr. D. H. Rendell, his research supervisor,from whom he learnt appreciably and drew constant encouragement. He wishes to thank Dr. S. W. Breckon, the Head of the Department, for his continued help and interest. The financial support , in the form of graduate fellowship was gratefully received from the Memorial University of Newfoundland. Almost all the physics needed for this work was learnt at Memorial. He, therefore, thanks all his teachers in the department of Physics of this university. Some points regarding the experimental side of the problem, became clear during the discussions with Dr. S. P. Reddy.